ENERGETIC ESTIMATES AND ASYMPTOTICS FOR ELECTRO–REACTION–DIFFUSION SYSTEMS

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1. Introduction

This paper is devoted to the investigation of equations modelling the migration of charged species in heterostructures via diffusion and reaction mechanisms. Such problems arise e.g. in semiconductor technology. An overview on model equations in this field may be found in Höfler and Strecker [10].

Our aim is to show that for such model equations the free energy along solutions decays monotonously and exponentially to its equilibrium value, i.e., that the models are correct from the thermodynamic point of view. The same result will be obtained for a discrete time scheme. The paper does not contain any existence results. These will be given in a forthcoming paper which will essentially make use of the physically motivated estimates of Theorem 4.1 and Theorem 5.3 below to find global a priori bounds which guarantee the existence of solutions.

The main tool in our investigations is an estimate of the free energy by the dissipation rate (see Theorem 5.2). Such estimates for reaction–diffusion equations for uncharged particles go back to Gröger [9]. For a special case with only one sort of charged dopants but using the local electroneutrality approximation analogous results have been obtained by Glitzky, Gröger and Hünlich [6], [7]. In this paper we present a general result for systems with arbitrarily many charged species which enables us to prove the exponential decay of the free energy to its equilibrium value along trajectories of the system.

The paper is organized as follows. In the remainder of this section we introduce the model which our considerations are based on, we give the notation and collect some basic results we need in our investigations. Section 2 is devoted to the precise analytical formulation of the problem including the basic assumptions. It also contains the definition of the physically motivated energy functionals and of the dissipation rate. In Section 3 we investigate the steady states. Under the Slater condition (3.3) we find exactly one steady state in the sense of (3.1). This state is related to the minimizers of certain convex functionals. Our first energetic estimates leading to the monotonicity and boundedness of the free energy along solutions of the system and to some conclusions concerning the boundedness of the electrostatic

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potential are collected in Section 4. Section 5 contains our main results. At first, for motivation, we show asymptotics for solutions which are known to be globally bounded from above and from below away from zero. Next, under the additional assumption (5.1) concerning the structure of the reaction system we prove an estimate of the difference of the free energy to its equilibrium value by the dissipation rate (Theorem 5.2). After this we obtain the asymptotics for solutions without using global upper and lower bounds. This is the essential new result in this paper. In Section 6 we show that for an implicit time discretization scheme the monotonous and exponential decay of the free energy to its equilibrium value remains true. Now let us introduce our mathematical model. We use the notation

X_i, $i = 1, \ldots, m$	–	mobile species
q_i	–	charges
u_i	–	concentrations
v_i	–	chemical potentials
$u_0 := \sum_{i=1}^m q_i\, u_i$	–	charge density of mobile species
v_0	–	electrostatic potential
$\zeta_i := v_i + q_i v_0$	–	electrochemical potentials
$a_i := e^{\zeta_i}$	–	electrochemical activities
j_i	–	mass fluxes.

The relation between concentrations and chemical potentials is assumed to be given by the Boltzmann statistics

$$u_i = \bar{u}_i\, e^{v_i}, \quad i = 1, \ldots, m,$$

where $\bar{u}_i$ are reference densities. Note, that in the case of heterostructures these reference densities generally depend on the space variable. The driving forces for the fluxes j_i are the gradients of the electrochemical potentials ζ_i. Thus the expressions for the fluxes j_i contain diffusion and drift terms

$$j_i = -D_i\, u_i \nabla \zeta_i = -D_i\, u_i \nabla (v_i + q_i v_0)$$

with diffusion coefficients D_i.
We consider mass action type reactions of the form

$$\alpha_1 X_1 + \cdots + \alpha_m X_m \rightleftharpoons \beta_1 X_1 + \cdots + \beta_m X_m, \quad (\alpha, \beta) \in \mathcal{R},$$

where (α, β) is a pair of vectors $(\alpha_1, \ldots \alpha_m)$, $(\beta_1, \ldots, \beta_m)$ of stoichiometric coefficients which characterizes the reaction from $\sum_{i=1}^m \alpha_i\, X_i$ to $\sum_{i=1}^m \beta_i\, X_i$ and its converse reaction. Thereby $\mathcal{R}$ describes the finite set of volume reactions under consideration. In principle, the reaction rate of a reaction (α, β) is proportional to terms of the form

$$\prod_{i=1}^m b_i^{\alpha_i} - \prod_{i=1}^m b_i^{\beta_i}$$

where b_i means some activity of the i–th species. From the literature and also by discussions with I. Rubinstein, G. Wachutka and others we could not decide if here the chemical activities $b_i = e^{v_i}$ or the electrochemical ones $b_i = a_i$ should be used.

Assuming that the charge during the reaction is conserved, i.e. $(\alpha - \beta) \cdot q = 0$, the difference between both versions is seen by

$$\prod_{i=1}^{m} e^{v_i \alpha_i} - \prod_{i=1}^{m} e^{v_i \beta_i} = e^{-\alpha \cdot q v_0} \Big(\prod_{i=1}^{m} a_i^{\alpha_i} - \prod_{i=1}^{m} a_i^{\beta_i} \Big)$$

which means that there occurs a factor depending on the electrostatic potential if $\alpha \cdot q \neq 0$. As in Gajewski and Gröger [5] we prefer to use the electrochemical activities but allow the relaxation constants to depend on the electrostatic potential

$$\begin{aligned} R_i(a, v_0) &= \sum_{(\alpha,\beta) \in \mathcal{R}} R_{\alpha\beta}(a, v_0)(\alpha_i - \beta_i), \\ R_{\alpha\beta}(a, v_0) &= \tilde{k}_{\alpha\beta}(\cdot, v_0) \Big(\prod_{k=1}^{m} a_k^{\alpha_k} - \prod_{k=1}^{m} a_k^{\beta_k} \Big) \end{aligned} \tag{1.1}$$

such that both versions are involved. Furthermore there may occur reactions on the boundary Γ of Ω. Similar to (1.1) we write

$$\begin{aligned} R_i^{\Gamma}(a, v_0) &= \sum_{(\alpha,\beta) \in \mathcal{R}^{\Gamma}} R_{\alpha\beta}^{\Gamma}(a, v_0)(\alpha_i - \beta_i), \\ R_{\alpha\beta}^{\Gamma}(a, v_0) &= \tilde{k}_{\alpha\beta}^{\Gamma}(\cdot, v_0) \Big(\prod_{k=1}^{m} a_k^{\alpha_k} - \prod_{k=1}^{m} a_k^{\beta_k} \Big) \end{aligned} \tag{1.2}$$

where $\mathcal{R}^{\Gamma}$ describes the finite set of the involved boundary reactions. By

$$\mathcal{S} := \operatorname{span}\{\alpha - \beta : (\alpha, \beta) \in \mathcal{R} \cup \mathcal{R}^{\Gamma}\} \subset \mathbb{R}^m$$

we denote the stoichiometric subspace belonging to the considered volume and boundary reactions.

The basic equations are the continuity equations for all species and the Poisson equation for the electrostatic potential

$$\begin{aligned} \frac{\partial u_i}{\partial t} + \nabla \cdot j_i + R_i = 0, \quad i = 1, \dots, m, \quad \text{on } \mathbb{R}_+ \times \Omega, \\ \nu \cdot j_i = R_i^{\Gamma}, \quad i = 1, \dots, m, \quad \text{on } \mathbb{R}_+ \times \Gamma; \\ -\nabla \cdot (\varepsilon \nabla v_0) = f + \sum_{i=1}^{m} q_i u_i \quad \text{on } \mathbb{R}_+ \times \Omega, \\ \nu \cdot (\varepsilon \nabla v_0) + \tau v_0 = f^{\Gamma} \quad \text{on } \mathbb{R}_+ \times \Gamma; \\ u_i(0) = U_i, \quad i = 1, \dots, m, \quad \text{on } \Omega \end{aligned}$$

where ε is the dielectric permittivity, τ represents a capacity of the boundary and the functions f and f^{Γ} are fixed source terms not depending on time.

From the above continuity equations follows the continuity equation for the charge density

$$\begin{aligned} \frac{\partial u_0}{\partial t} = \sum_{i=1}^{m} q_i \frac{\partial u_i}{\partial t} \text{ on } \mathbb{R}_+ \times \Omega, \\ u_0(0) = U_0 := \sum_{i=1}^{m} q_i U_i \text{ on } \Omega. \end{aligned}$$

Now we introduce several symbols and collect some basic results which we shall use in our considerations. Let be $u \in \mathbb{R}^m$. Then $u > 0$, $u \geq c$ means $u_i > 0$, $u_i \geq c$ for $i = 1, \dots, m$. If $\alpha \in \mathbb{Z}_+^m$ then u^α denotes the product $\prod_{i=1}^m u_i^{\alpha_i}$. For the scalar product in $\mathbb{R}^m$ we use a centered dot. If there is no danger of misunderstanding we shall write shortly L^p instead of $L^p(\Omega, \mathbb{R}^k)$, and H^1 instead of $H^1(\Omega, \mathbb{R}^k)$, $k \in \mathbb{N}$.

Since the regularity results of Gröger [8] for the Poisson equation which we need in our investigations work in the 2–dimensional case only, we restrict ourselves to the case $\Omega \subset \mathbb{R}^2$. Thus we can additionally make use of some helpful results of Trudinger [12].

Lemma 1.1. *Let $\Omega \subset \mathbb{R}^2$ be a bounded Lipschitz domain.*

i) *For each $\gamma > 0$ there exists a $c(\gamma)$ such that $\int_\Omega e^{|v|} dx$, $\int_\Gamma e^{|v|} d\Gamma \leq c(\gamma)$ if $v \in H^1(\Omega)$, $\|v\|_{H^1} \leq \gamma$.*

ii) *If $v \in H^1(\Omega)$ then $e^{|v|} \in L^p(\Omega)$, $e^{|v|} \in L^p(\Gamma)$ for all $p \in [1, \infty)$.*

Proof. The first assertion in i) follows directly from Trudinger [12]. The proof is based on the imbedding result of Trudinger

$$\|v\|_{L^q(\Omega)} \leq c(\Omega)\sqrt{q}\, \|v\|_{H^1(\Omega)}, \quad v \in H^1(\Omega), \quad q \geq 1$$

and on the Taylor expansion of the exponential function. For the second assertion in i) we use additionally the following imbedding result which can be derived from Kufner, John and Fučik [11]

$$\|v\|_{L^q(\Gamma)}^q \leq c(\Omega)\, q\, \|v\|_{L^{2(q-1)}(\Omega)}^{q-1} \|v\|_{H^1(\Omega)}, \quad v \in H^1(\Omega), \quad q \geq 2.$$

Let $v \in H^1(\Omega)$, $\|v\|_{H^1} \leq \gamma$. Then we estimate the boundary integral by

$$\begin{aligned}
\int_\Gamma e^{|v|} \mathrm{d}\Gamma &\leq \sum_{k=0}^\infty \frac{1}{k!}\, \|v\|_{L^k(\Gamma)}^k \\
&\leq 1 + \|v\|_{L^1(\Gamma)} + c \sum_{k=2}^\infty \frac{1}{k!}\, k\, \|v\|_{L^{2(k-1)}}^{k-1} \gamma \\
&\leq 1 + c\gamma + c \sum_{k=2}^\infty \frac{1}{k!} \gamma^k k \left(c\sqrt{2(k-1)}\right)^{k-1}.
\end{aligned}$$

The quotient criterion shows that this series converges and that the $L^1(\Gamma)$–norm of $e^{|v|}$ is bounded by a constant $c(\gamma)$. Assertion ii) is a consequence of assertion i). □

2. Formulation of the problem

Now we give a precise analytical description of the problem we want to discuss in the paper. We define function spaces, operators and physically motivated quantities like energy functionals and the dissipation rate.

At first we fix basic **assumptions** with respect to the data of the problem.

$$
\left.
\begin{aligned}
&\Omega \subset \mathbb{R}^2 \text{ bounded, Lipschitzian;}\\
&\bar u_i \in L^\infty(\Omega),\ \bar u_i \ge c > 0,\\
&U_i \in L^\infty(\Omega),\ U_i \ge 0,\\
&D_i \in L^\infty(\Omega),\ D_i \ge c > 0,\ i = 1, \dots, m;\\
&\tilde k_{\alpha\beta} \in \mathrm{Car}(\Omega \times \mathbb{R}), \quad \tilde k_{\alpha\beta}(x, y) \le c\, e^{c\,|y|} \text{ if } x \in \Omega,\ y \in \mathbb{R},\\
&\tilde k_{\alpha\beta}(x, y) \ge c_R > 0 \text{ if } x \in \Omega,\ y \in [-R, R],\\
&\tilde k^\Gamma_{\alpha\beta} \in \mathrm{Car}(\Gamma \times \mathbb{R}), \quad \tilde k^\Gamma_{\alpha\beta}(x, y) \le c\, e^{c\,|y|} \text{ if } x \in \Gamma,\ y \in \mathbb{R},\\
&\tilde k^\Gamma_{\alpha\beta}(x, y) \ge c_R > 0 \text{ if } x \in \Gamma,\ y \in [-R, R],\\
&(\alpha, \beta) \in \mathcal{R} \cup \mathcal{R}^\Gamma \subset \mathbb{Z}^m_+ \times \mathbb{Z}^m_+;\\
&q \in \mathbb{Z}^m,\ \alpha \cdot q = \beta \cdot q;\\
&\varepsilon \in L^\infty(\Omega),\ \varepsilon \ge c > 0,\ \tau \in L^\infty(\Gamma),\ \tau \ge c > 0,\\
&f \in L^\infty(\Omega),\ f^\Gamma \in L^\infty(\Gamma).
\end{aligned}
\right\} \tag{2.1}
$$

Remember that we have defined $U_0 := \sum_{i=1}^m q_i U_i$. For the weak formulation of our problem we use the variables

$$v = (v_0, v_1, \dots, v_m) \in \mathbb{R}^{m+1},\ \ u = (u_0, u_1, \dots, u_m) \in \mathbb{R}^{m+1},$$

$$\zeta = (\zeta_1, \dots, \zeta_m) \in \mathbb{R}^m \text{ where } \zeta_i = \zeta_{vi} := v_i + q_i v_0.$$

We introduce the function spaces

$$X := H^1(\Omega, \mathbb{R}^{m+1}),\ \ W := \{w \in X : w_i^+ \in L^\infty(\Omega)\,,\ i = 1, \dots, m\}$$

and define the operators $A\colon W \times X \longrightarrow X^*$, $E_0\colon H^1 \longrightarrow (H^1)^*$ and $E\colon X \longrightarrow X^*$ by

$$
\begin{aligned}
\langle A(w, v), \bar v\rangle := \int_\Omega \Big\{ &\sum_{i=1}^m D_i \bar u_i e^{w_i} \nabla\zeta_{vi} \nabla\zeta_{\bar v i}\\
&+ \sum_{(\alpha,\,\beta)\in\mathcal{R}} \tilde k_{\alpha\beta}(\cdot, v_0)\Big(e^{\alpha\cdot\zeta_w} - e^{\beta\cdot\zeta_w}\Big)(\alpha - \beta)\cdot\zeta_{\bar v}\Big\}\,\mathrm{d}x\\
&+ \int_\Gamma \sum_{(\alpha,\,\beta)\in\mathcal{R}^\Gamma} \tilde k^\Gamma_{\alpha\beta}(\cdot, v_0)\Big(e^{\alpha\cdot\zeta_w} - e^{\beta\cdot\zeta_w}\Big)(\alpha - \beta)\cdot\zeta_{\bar v}\,\mathrm{d}\Gamma,
\end{aligned}
$$

$$\langle E_0 v_0, \bar v_0\rangle := \int_\Omega \Big\{\varepsilon \nabla v_0 \nabla \bar v_0 - f\,\bar v_0\Big\}\,\mathrm{d}x + \int_\Gamma \Big\{\tau v_0 - f^\Gamma\Big\}\bar v_0\,\mathrm{d}\Gamma,$$

$$\langle E v, \bar v\rangle := \langle E_0 v_0, \bar v_0\rangle + \int_\Omega \sum_{i=1}^m \bar u_i e^{v_i} \bar v_i\,\mathrm{d}x.$$

The problem we shall be concerned with consists in finding a solution to

Problem (P):

$$\begin{aligned} u'(t) + A(v(t), v(t)) = 0, \quad u(t) = Ev(t) \text{ f.a.e. } t \in \mathbb{R}_+, \quad u(0) = U, \\ u \in H^1_{\mathrm{loc}}(\mathbb{R}_+, X^*), \quad v \in L^2_{\mathrm{loc}}(\mathbb{R}_+, X), \\ v_i^+ \in L^\infty_{\mathrm{loc}}(\mathbb{R}_+, L^\infty(\Omega)),\, i = 1, \ldots, m. \end{aligned} \tag{P}$$

The 0–th components of these equations represent the continuity equation for the charge density and the Poisson equation, respectively. By 1 we denote the function with the constant value 1 on Ω. We define

$$\mathcal{U} := \Big\{ u \in X^* \colon u_0 = \sum_{i=1}^m q_i u_i,\ (\langle u_1, 1\rangle, \ldots, \langle u_m, 1\rangle) \in \mathcal{S} \Big\} \tag{2.2}$$

and introduce its orthogonal complement

$$\mathcal{U}^\perp = \Big\{ v \in X \colon \nabla \zeta = 0,\ \zeta \in \mathcal{S}^\perp \text{ where } \zeta_i = v_i + q_i v_0,\ i = 1, \ldots, m \Big\}.$$

Note that $\langle u_i, 1\rangle = \int_\Omega u_i \,\mathrm{d}x$ if $u_i \in (H^1)^* \cap L^1(\Omega)$. By integrating the continuity equations over $(0, t) \times \Omega$ one easily verifies the following invariance property.

Lemma 2.1. *If (u, v) is a solution to (P) then $u(t) \in \mathcal{U} + U$ for all $t \in \mathbb{R}_+$.*

Next we define the energy functionals. We introduce the functional $\Phi \colon X \longrightarrow \overline{\mathbb{R}}$ where

$$\Phi(v) := \int_\Omega \Big\{ \frac{\varepsilon}{2} |\nabla v_0|^2 - f v_0 \Big\} \mathrm{d}x + \int_\Gamma \Big\{ \frac{\tau}{2} v_0^2 - f^\Gamma v_0 \Big\} \mathrm{d}\Gamma + \int_\Omega \sum_{i=1}^m \bar{u}_i \left(e^{v_i} - 1 \right) \mathrm{d}x.$$

Because of Lemma 1.1 we have dom $\Phi = X$. Moreover, the functional Φ is continuous, strictly convex and Gâteaux differentiable, hence subdifferentiable, and it holds $\partial \Phi = E$. By $F \colon X^* \longrightarrow \overline{\mathbb{R}}$ we denote its conjugate functional (see [2])

$$F(u) := \Phi^*(u) = \sup_{v \in X} \Big\{ \langle u, v \rangle - \Phi(v) \Big\}.$$

Then F is proper, lower semicontinuous and convex. It holds $u = Ev = \partial \Phi(v)$ if and only if $v \in \partial F(u)$. If $u \in X^*$ and $u = Ev$ then F can be calculated as

$$F(u) = \int_\Omega \Big\{ \frac{\varepsilon}{2} |\nabla v_0|^2 + \sum_{i=1}^m \Big\{ u_i (\ln \frac{u_i}{\bar{u}_i} - 1) + \bar{u}_i \Big\} \Big\} \mathrm{d}x + \int_\Gamma \frac{\tau}{2} v_0^2 \mathrm{d}\Gamma$$

where v_0 is the solution to $E_0 v_0 = u_0$. The value $F(u)$ can be interpreted as the free energy of the state u. We intend to find estimates for the values of the functional F along trajectories of the system (P). For this purpose an other physical quantity, the dissipation rate

$$\begin{aligned} D(v) :=& \Big\langle A(v, v), v \Big\rangle,\ v \in W, \\ D(v) =& \int_\Omega \Big\{ \sum_{i=1}^m D_i \bar{u}_i e^{v_i} |\nabla \zeta_i|^2 + \sum_{(\alpha,\, \beta) \in \mathcal{R}} \tilde{k}_{\alpha\beta}(\cdot, v_0) \Big(e^{\alpha \cdot \zeta} - e^{\beta \cdot \zeta} \Big) (\alpha - \beta) \cdot \zeta \Big\} \mathrm{d}x \\ &+ \int_\Gamma \sum_{(\alpha,\, \beta) \in \mathcal{R}^\Gamma} \tilde{k}^\Gamma_{\alpha\beta}(\cdot, v_0) \Big(e^{\alpha \cdot \zeta} - e^{\beta \cdot \zeta} \Big) (\alpha - \beta) \cdot \zeta \,\mathrm{d}\Gamma \end{aligned} \tag{2.3}$$

will play an important rôle.

3. Steady states

With regard to Lemma 2.1 it seems to be useful to discuss the steady states for Problem (P) which satisfy the invariance property stated in Lemma 2.1. These steady states of (P) are solutions to

$$A(v,v) = 0,\ u = Ev,\ u \in \mathcal{U} + U,\ v \in W. \tag{3.1}$$

We introduce a further functional $\Phi_0 \colon X \to \overline{\mathbb{R}}$,

$$\Phi_0(v) := \Phi(v) + I_{\mathcal{U}^\perp}(v) - \langle U, v\rangle\,,\ v \in X.$$

This functional is proper, lower semicontinuous and strictly convex. Because of Lemma 1.1 we obtain by the Moreau-Rockafellar theorem (see [2]) that

$$\partial\Phi_0(v) = Ev + \partial I_{\mathcal{U}^\perp}(v) - U,\ v \in X.$$

At first, we show that the steady states (3.1) correspond to the minimizers of the functional Φ_0 on X. Indeed, let (u,v) be a solution to (3.1). Then $D(v) = 0$ which yields $v \in \mathcal{U}^\perp$, $\Phi_0(v) < \infty$, $\partial I_{\mathcal{U}^\perp}(v) = \mathcal{U}$. Moreover we have $u = Ev$ and $u - U = \hat{u} \in \mathcal{U}$. Therefore we conclude that $0 = u - \hat{u} - U \in \partial\Phi_0(v)$ which means $\Phi_0(v) = \min_{w\in X}\ \Phi_0(w)$. On the other side, if v is the minimizer of Φ_0 then $v \in \mathcal{U}^\perp$, $0 \in \partial\Phi_0(v)$ and there exists $\hat{u} \in \partial I_{\mathcal{U}^\perp}(v) = \mathcal{U}$ with

$$Ev - \hat{u} - U = 0. \tag{3.2}$$

First, equation (3.2) yields

$$\int_\Omega \bar{u}_i e^{v_i} h \mathrm{d}x - \langle \hat{u}_i, h\rangle - \int_\Omega U_i h \mathrm{d}x = 0 \quad \forall h \in H^1(\Omega).$$

Since $e^{v_i} \in L^2(\Omega)$, $\bar{u}_i$, $U_i \in L^\infty(\Omega)$ we find that $\hat{u}_i \in L^2(\Omega)$ and therefore $\hat{u}_0 = \sum_{i=1}^m q_i\hat{u}_i \in L^2(\Omega)$. Moreover from (3.2) we conclude that $E_0v_0 = \hat{u}_0 + U_0$ and thus we obtain the boundedness of the electrostatic potential $v_0 \in L^\infty(\Omega)$ and of the chemical potentials $v_i = \zeta_i - q_iv_0 \in L^\infty(\Omega)$ since $\zeta = \text{const}$. Thus $v \in W$ and because of $v \in \mathcal{U}^\perp$ we have $A(v,v) = 0$. Therefore (Ev, v) is a steady state in the sense of (3.1).

In order to ensure the existence of steady states we need an additional assumption which represents some kind of a Slater condition:

$$\int_\Omega \sum_{i=1}^m U_i\kappa_i \mathrm{d}x > 0 \quad \forall \kappa \in \mathcal{S}^\perp,\ \kappa \geq 0,\ \kappa \neq 0. \tag{3.3}$$

Theorem 3.1. *Under the assumptions* (2.1) *and* (3.3) *there exists a unique steady state* (u^*, v^*). *The element* v^* *is the unique minimizer of* $\Phi - \langle U, \cdot\rangle$ *on* $\mathcal{U}^\perp$ *while* u^* *is the unique minimizer of* F *on* $\mathcal{U} + U$. *Furthermore*

$$u^*,\ v^* \in L^\infty(\Omega, \mathbb{R}^{m+1}),\ v^* \in L^\infty(\Gamma, \mathbb{R}^{m+1}),$$

$$u_i^* \geq c > 0 \ \textit{a.e. on}\ \Omega,\ a_i^* := e^{v_i^* + q_i v_0^*} > 0,\ i = 1, \ldots, m.$$

Proof. i) There will be a unique minimizer for Φ_0 if $\Phi_0(v) \to \infty$ for $\|v\|_X \to \infty$. Suppose the last property to be not fulfilled. Then there exist $R \in \mathbb{R}_+$, $v_n \in \mathcal{U}^\perp$ such that $\|v_n\|_X \to \infty$ and

$$\Phi_0(v_n) = \Phi(v_n) - \langle U, v_n \rangle \le R.$$

This implies

$$c\Big\{ \|v_{n0}\|^2_{H^1} + \sum_{i=1}^m \left\|v^+_{ni}\right\|^2_{L^2} \Big\} - \langle U, v_n \rangle \le R. \tag{3.4}$$

We set $w_n = \dfrac{v_n}{\|v_n\|_X}$, then $w_n \rightharpoonup \hat{w}$ in X and we obtain

$$c\Big\{ \|w_{n0}\|^2_{H^1} + \sum_{i=1}^m \left\|w^+_{ni}\right\|^2_{L^2} \Big\} \le \frac{R}{\|v_n\|^2_X} + \frac{\|U\|_{X^*}}{\|v_n\|_X} \to 0.$$

Thus $w_{n0} \to 0$ in $H^1(\Omega)$, $w^+_{ni} \to 0$ in $L^2(\Omega)$. Therefore we can conclude that $w_{ni} = w^+_{ni} - w^-_{ni} \rightharpoonup \hat{w}_i$ in $L^2(\Omega)$ which shows that $-\hat{w}_i \ge 0$. Since $w_n \in \mathcal{U}^\perp$, for $\eta_{ni} := w_{ni} + q_i w_{n0}$ we have $\nabla \eta_{ni} = 0$ and $\eta_n \in \mathcal{S}^\perp$. Together with $w_{n0} \to 0$ in $H^1(\Omega)$ we get $\nabla w_{ni} \to 0$ in $L^2(\Omega)$, $w_{ni} \to \hat{w}_i$ in $H^1(\Omega)$. Therefore we find $w_n \to \hat{w} = (0, \hat{w}_1, \ldots, \hat{w}_m)$ in X. Since $\mathcal{U}^\perp$ is closed in X we obtain $(\hat{w}_1, \ldots, \hat{w}_m) \in \mathcal{S}^\perp$ and because of $\|w_n\|_X = 1$ it holds $(\hat{w}_1, \ldots, \hat{w}_m) \ne 0$.
From (3.4) it follows that

$$-\langle U, w_n \rangle \le \frac{R}{\|v_n\|_X} \to 0.$$

In the limit it results

$$-\langle U, \hat{w} \rangle = -\int_\Omega \sum_{i=1}^m U_i \, \hat{w}_i \, \mathrm{d}x \le 0$$

which contradicts to assumption (3.3).
ii) Let (u^*, v^*) be the steady state. Then $v^* \in \partial F(u^*)$,

$$F(u) - F(u^*) \ge \langle u - u^*, v^* \rangle = 0 \quad \forall u \in \mathcal{U} + U$$

since $v^* \in \mathcal{U}^\perp$. If $u \in \mathcal{U} + U$ and $F(u) = F(u^*)$ then

$$\langle u, v^* \rangle = \langle u^*, v^* \rangle = F(u^*) + \Phi(v^*) = F(u) + \Phi(v^*)$$

such that $u = Ev^* = u^*$. Thus u^* is the unique minimizer of F on $\mathcal{U} + U$.
iii) We have already shown that the minimizer v of the functional Φ_0 is bounded, $v_i \in L^\infty(\Omega) \cap H^1(\Omega)$, $i = 0, \ldots, m$. Since $v_i \in H^1(\Omega)$ we can extend v_i to a function in $H^1_0(\mathbb{R}^2)$ with the same L^∞–bound. The absolute continuity leads to the L^∞–estimate on the boundary Γ. $\square$

Remarks:

i) The assumption (3.3) is necessary for the existence of a steady state in the sense of (3.1), too. For the proof let (u^*, v^*) be a steady state, $\kappa \in \mathcal{S}^\perp$, $\kappa \ge 0$, $\kappa \ne 0$. Then $u^* = Ev^*$, $u^* \in U + \mathcal{U}$, which yields

$$0 < u^*_i = U_i + \sum_{(\alpha,\beta) \in \mathcal{R} \cup \mathcal{R}^\Gamma} t_{\alpha\beta}(\alpha_i - \beta_i), \; i = 1, \ldots, m, \;\; \text{f.a.e. } x \in \Omega, \; t_{\alpha\beta} \in \mathbb{R}$$

and therefore, since $\alpha-\beta\in\mathcal{S}$ for all $(\alpha,\beta)\in\mathcal{R}\cup\mathcal{R}^\Gamma$,

$$0<\int_\Omega\sum_{i=1}^m u_i^*\kappa_i\mathrm{d}x=\int_\Omega\sum_{i=1}^m U_i\kappa_i\mathrm{d}x.$$

ii) If U fulfils (3.3) and $\tilde U\in\mathcal{U}+U$ then $\tilde U$ fulfils (3.3), too.

iii) If (u^*,v^*) is the steady state corresponding to U and $(\tilde u^*,\tilde v^*)$ is the steady state corresponding to $\tilde U$ then $(u^*,v^*)=(\tilde u^*,\tilde v^*)$ if and only if $U-\tilde U\in\mathcal{U}$.

4. Monotonicity and boundedness of the free energy

By means of the unique steady state (u^*,v^*) we define the functional $\Psi\colon X^*\longrightarrow\overline{\mathbb{R}}$,

$$\Psi(u):=F(u)-F(u^*)-\langle u-u^*,v^*\rangle. \tag{4.1}$$

As a sum of F and an affine function the functional Ψ is proper, lower semicontinuous and convex and we have $\Psi(u)\geq 0$, $\Psi(u^*)=0$. Let us remark that for $u\in\mathcal{U}+U$ (especially for $u=u(t)$ if (u,v) is a solution to (P), see Lemma 2.1) the last term vanishes such that $\Psi(u)=F(u)-F(u^*)$ represents the distance of the free energy to its equilibrium value $F(u^*)$. For $u\in X^*$ with $u=Ev$ we obtain

$$\Psi(u)=\int_\Omega\Big\{\sum_{i=1}^m\Big\{u_i(\ln\frac{u_i}{u_i^*}-1)+u_i^*\Big\}+\frac{\varepsilon}{2}|\nabla(v_0-v_0^*)|^2\Big\}\mathrm{d}x+\int_\Gamma\frac{\tau}{2}(v_0-v_0^*)^2\mathrm{d}\Gamma$$

where $E_0v_0=u_0$, $E_0v_0^*=u_0^*$, and for such u we get

$$\begin{aligned}c\Big\{\sum_{i=1}^m\Big\|\sqrt{u_i}-\sqrt{u_i^*}\Big\|_{L^2}^2+\|v_0-v_0^*\|_{H^1}^2\Big\}&\leq\Psi(u)\\ &\leq c\Big\{\sum_{i=1}^m\|u_i-u_i^*\|_{L^2}^2+\|v_0-v_0^*\|_{H^1}^2\Big\}\\ &\leq c\Big\{\sum_{i=1}^m\|u_i-u_i^*\|_{L^2}^2+\|u_0-u_0^*\|_{(H^1)^*}^2\Big\}.\end{aligned} \tag{4.2}$$

If (u,v) is a solution to (P) then $v(t)-v^*\in\partial\Psi(u(t))$ f.a.e. $t\in\mathbb{R}_+$ and by the Brézis formula [1] we obtain

$$\begin{aligned}&e^{\lambda t_2}\Psi(u(t_2))-e^{\lambda t_1}\Psi(u(t_1))\\ &\quad=\int_{t_1}^{t_2}e^{\lambda s}\Big\{\lambda\Psi(u(s))+\Big\langle u'(s),v(s)-v^*\Big\rangle\Big\}\,\mathrm{d}s\\ &\quad=\int_{t_1}^{t_2}e^{\lambda s}\Big\{\lambda\Psi(u(s))-\Big\langle A(v(s),v(s)),v(s)-v^*\Big\rangle\Big\}\,\mathrm{d}s\\ &\quad=\int_{t_1}^{t_2}e^{\lambda s}\Big\{\lambda\Psi(u(s))-D(v(s))\Big\}\,\mathrm{d}s\end{aligned} \tag{4.3}$$

since $\langle A(v,v),v^*\rangle=0$ because of $v^*\in\mathcal{U}^\perp$. Now we set in (4.3) $\lambda=0$. Since $D(v)\geq 0$ and $\Psi(u)=F(u)-F(u^*)$ for solutions to (P) we find

Theorem 4.1. *We assume (2.1) and (3.3). Let (u,v) be a solution to (P). Then*

$$F(u(t_2))\leq F(u(t_1))\quad\textit{for}\quad t_2\geq t_1\geq 0,$$

i.e., F decreases monotonously along any solution to (P). Additionally,

$$F(u(t)) \le F(U) \quad \forall t \ge 0, \ \|D(v)\|_{L^1(\mathbb{R}_+)} \le F(U) - F(u^*),$$

$$\|v_0 - v_0^*\|^2_{L^\infty(\mathbb{R}_+,H^1)} + \sum_{i=1}^m \|u_i(\ln(u_i/u_i^*) - 1) + u_i^*\|_{L^\infty(\mathbb{R}_+,L^1)} \le c$$

where c depends only on the data.

Lemma 4.1. *We assume* (2.1) *and* (3.3). *Then there exists a constant $c > 0$ such that for any solution (u, v) to (P)*

$$\|v_0\|_{L^\infty(\mathbb{R}_+,L^\infty(\Omega))}, \ \|v_0\|_{L^\infty(\mathbb{R}_+,L^\infty(\Gamma))} \le c.$$

Proof. Since by Theorem 4.1 the L^1–norms of $u_i \ln u_i$ are bounded for all t we have that also for the right hand side u_0 of the Poisson equation $E_0 v_0 = u_0$ the L^1–norm of $u_0 \ln |u_0|$ is bounded for all t. Thus regularity results of Gröger [8] for elliptic boundary value problems imply that

$$\|v_0\|_{L^\infty(\mathbb{R}_+,L^\infty(\Omega))} \le c.$$

The estimate on the boundary is proved as in Theorem 3.1. □

5. Exponential decay of the free energy

In what follows we are looking for sharper estimates which express the exponential decay of the free energy to its equilibrium value along trajectories of the system (P). First let us start with a result for *nice* solutions which are a priori known to be bounded from above and from below away from zero.

Theorem 5.1. *We assume* (2.1) *and* (3.3). *Let (u, v) be a solution to (P) such that*

$$\frac{1}{R} \le u_i(t, x) \le R \ \text{a.e. on } \mathbb{R}_+ \times \Omega, \ i = 1, \dots, m, \ R > 0.$$

Then there exists a $\lambda(R) > 0$ such that

$$F(u(t)) - F(u^*) \le e^{-\lambda(R)t}(F(U) - F(u^*)) \quad \forall t \in \mathbb{R}_+$$

i.e., F decays exponentially to its equilibrium value along such a solution.

Proof. i) Under the assumptions of Theorem 5.1 we have

$$v_i = \ln \frac{u_i}{\bar{u}_i}, \ |v_i| \le c(R), \ |u_i - u_i^*| \le c(R)\,|v_i - v_i^*| \text{ a.e. on } \mathbb{R}_+ \times \Omega.$$

ii) By monotonicity arguments we obtain

$$\begin{aligned} c(R) \sum_{i=1}^m \|u_i - u_i^*\|^2_{L^2} &\le \int_\Omega \sum_{i=1}^m \bar{u}_i\,(e^{v_i} - e^{v_i^*})(v_i - v_i^*)\,\mathrm{d}x \\ &\le \langle Ev - Ev^*, v - v^* \rangle = \langle u - u^*, v - v^* \rangle. \end{aligned}$$

Since $\mathcal{S}^\perp \subset H^1(\Omega, \mathbb{R}^m)$ we can use the orthogonal decomposition

$$\zeta = \zeta' + \zeta'', \ \zeta' \in H^1(\Omega, \mathbb{R}^m) \ominus \mathcal{S}^\perp, \ \zeta'' \in \mathcal{S}^\perp.$$

Because of $u-u^*\in\mathcal{U}$ and $\zeta^*\in\mathcal{S}^\perp$ we continue our estimate by

$$\begin{aligned}\langle u-u^*,v-v^*\rangle &= \langle u_0-u_0^*,v_0-v_0^*\rangle+\sum_{i=1}^m\langle u_i-u_i^*,v_i-v_i^*\rangle\\ &= \sum_{i=1}^m\langle u_i-u_i^*,\zeta_i-\zeta_i^*\rangle = \int_\Omega\sum_{i=1}^m(u_i-u_i^*)\zeta_i'\,\mathrm{d}x\\ &\le \sum_{i=1}^m\|u_i-u_i^*\|_{L^2}\;\|\zeta_i'\|_{L^2}\,.\end{aligned}$$

Thus we get $\sum_{i=1}^m\|u_i-u_i^*\|_{L^2}\le c(R)\sum_{i=1}^m\|\zeta_i'\|_{L^2}$ and therefore from (4.2) it follows that

$$\Psi(u)\le c(R)\sum_{i=1}^m\|\zeta_i'\|_{L^2}^2\,.$$

iii) The dissipation rate $D(v)$ may be estimated from below by the following expression

$$D(v)\ge c(R)\Big\{\sum_{i=1}^m\|\nabla\zeta_i'\|_{L^2}^2+\int_\Omega\sum_{(\alpha,\beta)\in\mathcal{R}}\big((\alpha-\beta)\cdot\zeta'\big)^2\,\mathrm{d}x \\ +\int_\Gamma\sum_{(\alpha,\beta)\in\mathcal{R}^\Gamma}\big((\alpha-\beta)\cdot\zeta'\big)^2\,\mathrm{d}\Gamma\Big\}.$$

iv) One easily proves this Poincaré–like inequality: There exists a constant $c_0>0$ such that for all $\zeta'\in H^1(\Omega,\mathbb{R}^m)\ominus\mathcal{S}^\perp$

$$\sum_{i=1}^m\|\nabla\zeta_i'\|_{L^2}^2+\int_\Omega\sum_{(\alpha,\beta)\in\mathcal{R}}\big((\alpha-\beta)\cdot\zeta'\big)^2\,\mathrm{d}x \\ +\int_\Gamma\sum_{(\alpha,\beta)\in\mathcal{R}^\Gamma}\big((\alpha-\beta)\cdot\zeta'\big)^2\,\mathrm{d}\Gamma\ge c_0\sum_{i=1}^m\|\zeta_i'\|_{H^1}^2\,.$$

v) Combining the results of the previous steps we have the existence of a constant $c(R)$ such that

$$\Psi(u(s))\le c(R)\,D(v(s))\ \text{f.a.e. } s\in\mathbb{R}_+.$$

Using now (4.3) with $\lambda=\dfrac{1}{c(R)}$ the proof is complete. $\square$

To prove such asymptotic results for solutions to (P) where no upper and lower bounds are a priori known we need an additional assumption concerning the structure of the reaction system. At first we define the set $\mathcal{M}$

$$\mathcal{M}:=\Big\{a\in\mathbb{R}_+^m,\ v_0\in H^1(\Omega)\colon a^\alpha=a^\beta\ \forall(\alpha,\beta)\in\mathcal{R}\cup\mathcal{R}^\Gamma,\\ (E_0v_0,u_1,\dots,u_m)\in\mathcal{U}+U\text{ where } u_i:=\bar u_i\,a_i\,e^{-q_iv_0},\ i=1,\dots,m\Big\}.$$

If (u,v) is a steady state of (P) in the sense of (3.1) then $D(v)=0$, $\nabla\zeta=0$ and $\zeta\in\mathcal{S}^\perp$. Defining $a_i:=e^{\zeta_i}=\text{const}>0$ we obtain that $a^\alpha=a^\beta$ for all $(\alpha,\beta)\in\mathcal{R}\cup\mathcal{R}^\Gamma$. Furthermore it holds $(E_0v_0,u_1,\dots,u_m)\in\mathcal{U}+U$. Thus $a>0$

and $(a, v_0) \in \mathcal{M}$. On the other hand, if $(a, v_0) \in \mathcal{M}$ *and* $a > 0$ then defining $v_i := \ln a_i - q_i v_0$, $u_i := \bar{u}_i\, a_i\, e^{-q_i v_0}$, $i = 1, \dots, m$, $u_0 := E_0 v_0$ we find that (u, v) is a steady state of Problem (P) in the sense of (3.1).

Obviously, if $\mathcal{M}$ contains elements (a, v_0) with $a \notin \operatorname{int} \mathbb{R}^m_+$ then there is no correspondence of such an element to a steady state (u, v) of (P). This is caused by the fact that a vector u some components of which vanish on sets of positive measure does not lie in the image of the operator E. In the proof of the following theorems we need this correspondence between the steady state and the set $\mathcal{M}$, therefore we shall suppose that

$$\mathcal{M} \subset \operatorname{int} \mathbb{R}^m_+ \times H^1(\Omega). \tag{5.1}$$

From this additional assumption it follows $\mathcal{M} = \{a^*, v_0^*\}$ and we are able to prove the following estimate of the free energy by the dissipation rate which is the essential key for obtaining the exponential decay of the free energy along any solution to Problem (P).

Theorem 5.2. *Let* (2.1), (3.3) *and* (5.1) *be satisfied. Then for every* $R > 0$ *there exists a* $c_R > 0$ *such that*

$$F(Ev) - F(u^*) \le c_R D(v)$$

for all $v \in M_R$ *where*

$$M_R := \Big\{ v \in W:\ F(Ev) - F(u^*) \le R,\ Ev \in \mathcal{U} + U \Big\}.$$

Proof. i) Let $v \in M_R$. Then the potentials and activities have the following properties:

$$\|v_0\|_{L^\infty(\Omega)} \le c(R),\ v_i^+,\ \zeta_i^+ \in L^\infty(\Omega),\ a_i \in H^1(\Omega),\ a_i > 0,\ \sqrt{a_i/a_i^*} \in H^1(\Omega).$$

Since $\zeta^* = \text{const}$, $\zeta^* \in \mathcal{S}^\perp$ and $e^{\alpha\cdot\zeta^*} = e^{\beta\cdot\zeta^*}$ we find for the dissipation rate defined in (2.3) that

$$\begin{aligned} D(v) = \int_\Omega \Big\{ & \sum_{i=1}^m D_i u_i^* e^{v_i - v_i^*} |\nabla(\zeta_i - \zeta_i^*)|^2 \\ & + \sum_{(\alpha,\,\beta)\in\mathcal{R}} \tilde{k}_{\alpha\beta}(\cdot, v_0)\, e^{\alpha\cdot\zeta^*} \Big(e^{\alpha\cdot(\zeta-\zeta^*)} - e^{\beta\cdot(\zeta-\zeta^*)} \Big) (\alpha - \beta)\cdot(\zeta - \zeta^*) \Big\}\, \mathrm{d}x \\ & + \int_\Gamma \sum_{(\alpha,\,\beta)\in\mathcal{R}^\Gamma} \tilde{k}^\Gamma_{\alpha\beta}(\cdot, v_0)\, e^{\alpha\cdot\zeta^*} \Big(e^{\alpha\cdot(\zeta-\zeta^*)} - e^{\beta\cdot(\zeta-\zeta^*)} \Big) (\alpha - \beta)\cdot(\zeta - \zeta^*)\, \mathrm{d}\Gamma. \end{aligned}$$

Because of

$$e^{v_i - v_i^*} |\nabla(\zeta_i - \zeta_i^*)|^2 = e^{-q_i(v_0 - v_0^*)}\, e^{\zeta_i - \zeta_i^*} |\nabla(\zeta_i - \zeta_i^*)|^2 \ge c\, e^{-q_i(v_0 - v_0^*)} \left| \nabla \sqrt{e^{\zeta_i - \zeta_i^*}} \right|^2,$$

$$\left(e^{z_1} - e^{z_2}\right)\, (z_1 - z_2) \ge c\, \left| \sqrt{e^{z_1}} - \sqrt{e^{z_2}} \right|^2$$

we find a $c_0(R) > 0$ (depending on R since the L^∞–norm of v_0 depends on R) such that

$$D(v) \ge c_0(R)\, \tilde{D}(a) \tag{5.2}$$

where

$$\tilde{D}(a) = \int_\Omega \Big\{ \sum_{i=1}^m \Big|\nabla\sqrt{a_i/a_i^*}\Big|^2 + \sum_{(\alpha,\beta)\in\mathcal{R}} \Big[\prod_{i=1}^m \sqrt{a_i/a_i^*}^{\,\alpha_i} - \prod_{i=1}^m \sqrt{a_i/a_i^*}^{\,\beta_i}\Big]^2\Big\}\,\mathrm{d}x$$

$$+ \int_\Gamma \sum_{(\alpha,\beta)\in\mathcal{R}^\Gamma} \Big[\prod_{i=1}^m \sqrt{a_i/a_i^*}^{\,\alpha_i} - \prod_{i=1}^m \sqrt{a_i/a_i^*}^{\,\beta_i}\Big]^2 \mathrm{d}\Gamma.$$

Using the variables $w_i := \sqrt{a_i/a_i^*} - 1$ and a binomial expansion we get

$$\tilde{D}(a) = \sum_{i=1}^m \|\nabla w_i\|_{L^2}^2 + Q(w), \quad Q(w) := Q_1(w) + Q_2(w)$$

with

$$Q_1(w) = \int_\Omega \sum_{(\alpha,\beta)\in\mathcal{R}} ((\alpha-\beta)\cdot w)^2\,\mathrm{d}x + \int_\Gamma \sum_{(\alpha,\beta)\in\mathcal{R}^\Gamma} ((\alpha-\beta)\cdot w)^2\,\mathrm{d}\Gamma,$$

$$|Q_2(w)| \le c\,\left(\|w\|_{H^1}^3 + \|w\|_{H^1}^{p_0}\right)$$

where

$$p_0 = \max\Big\{3,\ 2\max_{(\alpha,\beta)\in\mathcal{R}\cup\mathcal{R}^\Gamma} \sum_{i=1}^m \alpha_i,\ 2\max_{(\alpha,\beta)\in\mathcal{R}\cup\mathcal{R}^\Gamma} \sum_{i=1}^m \beta_i\Big\}.$$

On the other hand, for $u := Ev$ we find

$$\sqrt{u_i/u_i^*} - 1 = e^{-q_i(v_0-v_0^*)/2}\,w_i + e^{-q_i(v_0-v_0^*)/2} - 1,\ i = 1,\dots,m.$$

By (4.2) this together with $u - u^* \in \mathcal{U}$ yields

$$c(R)\Big\{\sum_{i=1}^m \|w_i\|_{L^2}^2 + \|v_0 - v_0^*\|_{H^1}^2\Big\} \le \Psi(u) \le c\sum_{i=1}^m \|u_i - u_i^*\|_{L^2}^2\,. \tag{5.3}$$

It remains to show that for every $R > 0$ there exists a $\tilde{c}_R > 0$ such that

$$\Psi(u) < \tilde{c}_R\,\tilde{D}(a) \quad \forall v \in M_R,\ v \ne v^* \quad \text{(with } u,\ a \text{ corresponding to } v\text{)}.$$

ii) Suppose this assertion to be false. Then there exist $R > 0$ and sequences $c_n \in \mathbb{R}$, $v_n \in M_R$ with corresponding u_n, a_n such that $c_n \to \infty$ and

$$R \ge \Psi(u_n) \ge c_n \tilde{D}(a_n) > 0.$$

Set $\lambda_n := \sqrt{\Psi(u_n)}$ and $w_{ni} := \sqrt{a_{ni}/a_i^*} - 1$. Then

$$R \ge {\lambda_n}^2 \ge c_n\Big\{\sum_{i=0}^m \|\nabla w_{ni}\|_{L^2}^2 + Q(w_n)\Big\}. \tag{5.4}$$

First, this implies $\nabla w_{ni} \to 0$ in L^2, and since $\|w_n\|_{L^2}^2 \le c(R)$ (cf. the left hand side of (5.3)) we may assume that w_n converges in H^1 to a constant vector $\hat{w} \in \mathbb{R}^m$. Next, Fatou's lemma ensures that

$$Q(\hat{w}) \le \liminf_{n\to\infty} Q(w_n) = 0$$

and defining $\hat{a}_i := a_i^*(1+\hat{w}_i)^2$, $i = 1,\dots,m$, we obtain

$$\hat{a}^\alpha = \hat{a}^\beta \quad \forall\,(\alpha,\beta) \in \mathcal{R}\cup\mathcal{R}^\Gamma.$$

Again the left hand side of (5.3) gives

$$\|v_{n0} - v_0^*\|_{H^1} \leq c(R).$$

Thus, at least for a subsequence, $v_{n0} \rightharpoonup \hat{v}_0$ in H^1, $v_{n0} \to \hat{v}_0$ in L^2, $L^2(\Gamma)$, $E_0 v_{n0} \rightharpoonup E_0 \hat{v}_0$ in $(H^1)^*$. Defining

$$\hat{u}_i := \bar{u}_i \hat{a}_i e^{-q_i \hat{v}_0} = u_i^* \frac{\hat{a}_i}{a_i^*} e^{-q_i(\hat{v}_0 - v_0^*)},\ i = 1, \ldots, m,$$

we get

$$\|u_{ni} - \hat{u}_i\|_{L^2} \leq c(R) \Big\{ \|w_{ni} - \hat{w}_i\|_{L^4}^2 + \|w_{ni} - \hat{w}_i\|_{L^2} + \|v_{n0} - \hat{v}_0\|_{L^2} \Big\} \to 0$$

and $Ev_n \rightharpoonup (E_0 \hat{v}_0, \hat{u}_1, \ldots, \hat{u}_m)$ in X^*. Since $\mathcal{U} + U$ is weakly closed we find

$$(E_0 \hat{v}_0, \hat{u}_1, \ldots, \hat{u}_m) \in \mathcal{U} + U.$$

By the definition of $\mathcal{M}$ we obtain

$$(\hat{a}, \hat{v}_0) \in \mathcal{M}. \tag{5.5}$$

Now assumption (5.1) implies that $\hat{a} = a^*$, $\hat{v}_0 = v_0^*$ and consequently, $\hat{u} = u^*$. From the right hand side of (5.3) we then conclude that $\lambda_n \to 0$.

iii) We set $b_{ni} := \dfrac{w_{ni}}{\lambda_n}$, $y_{ni} := \dfrac{u_{ni} - u_i^*}{\lambda_n}$, $i = 1, \ldots, m$, $z_n := \dfrac{v_{n0} - v_0^*}{\lambda_n}$. Because of (5.4) we get

$$\frac{1}{c_n} \geq \sum_{i=1}^m \|\nabla b_{ni}\|_{L^2}^2 + Q_1(b_n) + \frac{1}{{\lambda_n}^2} Q_2(\lambda_n\, b_n).$$

This implies $\nabla b_{ni} \to 0$ in L^2 and since $\|b_n\|_{L^2}^2 \leq c(R)$ (see (5.3)) we may assume that b_n converges in H^1 to a constant $\hat{b} \in \mathbb{R}^m$. Moreover

$$\frac{1}{{\lambda_n}^2}\ |Q_2(\lambda_n\, b_n)| \leq c\ \left(\lambda_n\, \|b_n\|_{H^1}^3 + {\lambda_n}^{p_0 - 2}\, \|b_n\|_{H^1}^{p_0}\right) \to 0.$$

Therefore $Q_1(\hat{b}) = 0$ which means $\hat{b} \in S^\perp$. From (5.3) we have $\|z_n\|_{H^1} \leq c(R)$ such that, for a subsequence, $z_n \rightharpoonup \hat{z}$ in H^1, $z_n \to \hat{z}$ in L^2, $L^2(\Gamma)$ as well as $E_0 z_n \rightharpoonup E_0 \hat{z}$ in $(H^1)^*$. Defining

$$\hat{y}_i := u_i^*(2\hat{b}_i - q_i \hat{z}),\ i = 1, \ldots, m,$$

we obtain

$$\|y_n - \hat{y}\|_{L^2} \leq c(R) \Big\{ \left\|b_n - \hat{b}\right\|_{L^2} + \|z_n - \hat{z}\|_{L^2} + \lambda_n \Big\} \to 0$$

and $(E_0 \hat{z} - E_0 0, \hat{y}_1, \ldots, \hat{y}_m) \in \mathcal{U}$ since $(E_0 z_n - E_0 0, y_{n1}, \ldots, y_{nm}) \in \mathcal{U}$. Because of $\hat{b} \in \mathcal{S}^\perp$ we find $(\hat{z}, 2\hat{b}_1 - q_1 \hat{z}, \ldots, 2\hat{b}_m - q_m \hat{z}) \in \mathcal{U}^\perp$ and from this

$$\langle E_0 \hat{z} - E_0 0, \hat{z} \rangle + \int_\Omega \sum_{i=1}^m u_i^* (2\hat{b}_i - q_i \hat{z})^2 \mathrm{d}x = 0.$$

This implies $\hat{z}=0$, $\hat{b}=0$, consequently $\hat{y}=0$. On the other hand, because of the right hand side of (5.3) it holds

$$1 \le c \sum_{i=1}^{m} \|y_{ni}\|_{L^2}^2 \to 0$$

which yields the contradiction. $\square$

Theorem 5.2 gives the possibility to prove asymptotics for *any* solution.

Theorem 5.3. *Let* (2.1), (3.3) *and* (5.1) *be satisfied. Then there exists a* $\lambda > 0$ *such that*

$$F(u(t)) - F(u^*) \le e^{-\lambda t}\,(F(U) - F(u^*)) \quad \forall t \ge 0, \tag{5.6}$$

for any solution (u,v) *to (P), i.e.,* F *decays exponentially to its equilibrium value along any trajectory. Moreover for some* $c>0$ *depending only on the data it holds*

$$\begin{gathered} \left\|\sqrt{u_i(t)/u_i^*} - 1\right\|_{L^2}, \left\|\sqrt{a_i(t)/a_i^*} - 1\right\|_{L^2}, \|v_0(t) - v_0^*\|_{H^1} \le c\,e^{-\lambda t/2}, \\ \|u_i(t)/u_i^* - 1\|_{L^1} \le c\,e^{-\lambda t/2},\ i=1,\dots,m,\ \forall t \ge 0. \end{gathered} \tag{5.7}$$

Proof. Let (u,v) be any solution to (P) and $R := \Psi(U)$. Then $v(s) \in M_R$ f.a.e. s and

$$\Psi(u(s)) \le c_R\, D(v(s)) \text{ f.a.e. } s.$$

Setting now $\lambda = \dfrac{1}{c_R}$ in (4.3) we obtain (5.6) which means the exponential decay of the free energy to its equilibrium value along this trajectory. The first three inequalities of (5.7) then follow directly from (4.2) and (5.3), respectively. For the last estimate in (5.7) we use

$$\|u_i(t)/u_i^* - 1\|_{L^1} \le \left\|\sqrt{u_i(t)/u_i^*} - 1\right\|_{L^2} \left\|\sqrt{u_i(t)/u_i^*} + 1\right\|_{L^2}$$

and the global boundedness of the L^2–norm of $\sqrt{u_i(t)}$ (see Theorem 4.1). $\square$

Corollary 5.1. *Let* (2.1), (3.3) *and* (5.1) *be satisfied. Then there exists a* $c>0$ *such that*

$$\begin{gathered} \|v_0 - v_0^*\|_{L^2(\mathbb{R}_+,H^1)}, \|v_0 - v_0^*\|_{L^1(\mathbb{R}_+,L^1)}, \|v_0 - v_0^*\|_{L^1(\mathbb{R}_+,L^1(\Gamma))} \le c, \\ \|u_i/u_i^* - 1\|_{L^1(\mathbb{R}_+,L^1)}, \|u_i/u_i^* - 1\|_{L^1(\mathbb{R}_+,L^1(\Gamma))} \le c,\ i=1,\dots,m, \end{gathered}$$

for any solution (u,v) *to (P).*

Proof. The first three estimates follow directly from the third inequality of (5.7) by taking into account the continuous imbedding of $H^1(\Omega)$ into $L^1(\Omega)$ and $L^1(\Gamma)$. For the fourth estimate we use the last inequality of (5.7). By the L^∞ –estimates for v_0 and v_0^* we have

$$\begin{aligned} |u_i/u_i^* - 1| &\le c\Big(|a_i/a_i^* - 1| + |v_0 - v_0^*|\Big) \\ &\le c\Big(\Big|\sqrt{a_i/a_i^*} - 1\Big|^2 + \Big|\sqrt{a_i/a_i^*} - 1\Big| + |v_0 - v_0^*|\Big), \end{aligned}$$

because of $u_i/u_i^* \in H^1$ therefore

$$\|u_i/u_i^* - 1\|_{L^1(\Gamma)} \le c\Big\{ \Big\|\sqrt{a_i/a_i^*} - 1\Big\|_{H^1}^2 + \Big\|\sqrt{a_i/a_i^*} - 1\Big\|_{L^2}^{2/3} + \|v_0 - v_0^*\|_{H^1} \Big\}.$$

Since by Theorem 4.1 $\|D(v)\|_{L^1(\mathbb{R}_+)} \le c$ we find by (5.2) that the norm of $\sqrt{a_i/a_i^*} - 1$ is bounded in $L^2(\mathbb{R}_+, H^1)$. This together with (5.7) proves the last inequality of the corollary. □

Remark. The proof of the exponential decay of the free energy to its equilibrium value along solutions as in Theorem 5.3, i.e. without using the global upper and lower boundedness of the concentrations, for reaction diffusion processes of uncharged particles may be found in Gröger [9]. For a special reaction diffusion model arising in semiconductor technology which uses only one sort of charged dopants as well as the local electroneutrality approximation analogous estimates have been obtained in Glitzky, Gröger and Hünlich [6], [7]. Gajewski and Gärtner [3] have proved such results for the van Roosbroeck equations including magnetic field effects, too.

Remark. There are reaction systems where assumption (5.1) is not fulfilled (see [9] for examples). Whether the assertions of Theorem 5.3 are valid only assuming (3.3) remains an open question.

Remark. If the reaction diffusion system (P) does not fulfil the assumption (5.1) there is at least the possibility to prove the exponential decay of the free energy to its equilibrium value under the assumption that the initial value U lies sufficiently near to the equilibrium value u^*. Let d be defined by

$$d := \inf \Big\{ F(u) - F(u^*) \,\Big|\, u_i = \bar{u}_i a_i e^{-q_i v_0},\ i = 1, \dots, m,$$
$$(a, v_0) \in \mathcal{M},\ a \in \partial\mathbb{R}_+^m \Big\}.$$

Note that $\inf \emptyset = +\infty$. Therefore, if (5.1) is fulfilled then $\mathcal{M}$ corresponds to the steady state of (P) and $d = +\infty$. We now replace (5.1) by the assumption, that for the given initial value U

$$F(U) - F(u^*) < d. \tag{5.8}$$

Then Theorem 5.2 may be reformulated as follows.

Theorem 5.4. *Let* (2.1), (3.3) *and* (5.8) *be satisfied. Then for every R belonging to the interval* $(0, F(U) - F(u^*)]$ *there exists a $c_R > 0$ such that*

$$F(Ev) - F(u^*) \le c_R D(v)$$

for all $v \in M_R$ where

$$M_R := \Big\{ v \in W\colon\ F(Ev) - F(u^*) \le R,\ Ev \in \mathcal{U} + U \Big\}.$$

Proof. The proof of Theorem 5.2 must be changed in the following way. Up to (5.5) the proof is exactly the same. We arrive at $(\hat{a}, \hat{v}_0) \in \mathcal{M}$. Since Ψ is lower semicontinuous, $u_{ni} \to \hat{u}_i$ in $L^2(\Omega)$, we obtain from $\Psi(u_n) \le R < d$ that

$$\Psi(\hat{u}) \le \liminf_{n\to\infty} \Psi(u_n) \le R < d.$$

Thus $(\hat{a}, \hat{v}_0) \notin \left(\partial\mathbb{R}^m_+ \times H^1(\Omega)\right) \cap \mathcal{M}$ and therefore $\hat{a} = a^*$, $\hat{v}_0 = v_0^*$, $\hat{u} = u^*$. The following argumentation is exactly the same as in Theorem 5.2. □

The results of Theorem 5.3 and its corollary remain true, too, if the assumption (5.1) is replaced by (5.8).

Remark. The results of this paper, Theorem 4.1 and Theorem 5.3, can be used to prove a priori estimates and the existence of solutions to (P). A priori estimates for the concentrations u from above can be found by the first energetic estimate Theorem 4.1 and Moser technique (see [4] for the van Roosbroeck system and [5] for general systems as considered here). In a forthcoming paper we shall prove the existence of a priori lower bounds for the concentrations u away from zero (in [5] this property seems to remain unproved since in contrary to [4] no Dirichlet boundary conditions as well as more general reaction terms are involved). The integrability properties of Corollary 5.1 following from Theorem 5.3 enable us to show that $\ln u_i$, $i = 1, \ldots, m$, may be estimated in $L^\infty(\mathbb{R}_+, L^1)$ by a constant only depending on the data. By Moser iteration the desired lower bounds are obtained.

6. Discrete–time problems

Our aim is to approximate problem (P) by a discrete–time problem which saves the important property of monotonous and exponential decay of the free energy along trajectories of the discrete–time system to its equilibrium value. This means, we look for a discrete–time problem which is correct from the thermodynamic point of view, too.

We assume that we are given sequences of partitions $\{Z_n\}_{n\in\mathbb{N}}$ of $\mathbb{R}_+$,

$$Z_n = \left\{t_n^0, t_n^1, \ldots, t_n^k, \ldots\right\},\ t_n^0 = 0,\ t_n^k \in \mathbb{R}_+,\ t_n^{k-1} < t_n^k,\ k \in \mathbb{N},\ t_n^k \to +\infty \text{ as } k \to \infty.$$

Let

$$h_n^k := t_n^k - t_n^{k-1},\ S_n^k := (t_n^{k-1}, t_n^k],\ \bar{h}_n := \sup_{k\in\mathbb{N}} h_n^k.$$

For a given partition Z_n of $\mathbb{R}_+$ and a given Banach space B we introduce the space of piecewise constant functions

$$C_n(\mathbb{R}_+, B) := \Big\{u : \mathbb{R}_+ \longrightarrow B \,:\, u(t) = u^k \quad \forall t \in S_n^k,\ u^k \in B,\ k \in \mathbb{N}\Big\}.$$

We define the difference operator $\Delta_n : C_n(\mathbb{R}_+, X^*) \longrightarrow C_n(\mathbb{R}_+, X^*)$ by

$$(\Delta_n u)^k := \frac{1}{h_n^k}(u^k - u^{k-1}),\ u^0 := U$$

where U is the initial value of problem (P). For $n \in \mathbb{N}$, we investigate the problem

$$\begin{gathered} \Delta_n u_n + A(v_n, v_n) = 0,\ u_n = E v_n, \\ v_n \in C_n(\mathbb{R}_+, X),\ v_{ni}^+ \in C_n(\mathbb{R}_+, L^\infty(\Omega)),\ i = 1, \ldots, m. \end{gathered} \tag{P$_n$}$$

This fully implicit scheme can be written in more detail as

$$u_n^k + h_n^k A(v_n^k, v_n^k) = u_n^{k-1},\ u_n^k = E v_n^k,\ v_n^k \in W,\ k \in \mathbb{N},\ u_n^0 = U.$$

First, let us note that the discrete–time problems (P_n) fulfil the same invariance property

$$u_n(t) \in \mathcal{U} + U \quad \forall t \in \mathbb{R}_+ \tag{6.1}$$

as the continuous problem (P). This assertion follows easily by integrating the discrete equations over $(0, t_n^k) \times \Omega$, $k \in \mathbb{N}$. Furthermore, the discrete–time problems (P_n) have the same steady state (u^*, v^*) as the continuous problem (P).

Theorem 6.1. *We assume* (2.1) *and* (3.3)*. Let $h > 0$ be given and let Z_n be any partition of $\mathbb{R}_+$ with $\bar{h}_n \le h$. Then the free energy decreases monotonously along any solution (u_n, v_n) to the discrete–time problem (P_n), i.e.,*

$$F(u_n(t_2)) \le F(u_n(t_1)) \le F(U) \quad \textit{for} \quad t_2 \ge t_1 \ge 0.$$

Additionally, if (5.1) *or* (5.8) *is satisfied then there exists a $\lambda > 0$ such that*

$$F(u_n(t)) - F(u^*) \le e^{-\lambda t}(F(U) - F(u^*)) \quad \forall t \ge 0$$

for any solution (u_n, v_n) to (P_n).

Proof. Let (u_n, v_n) be a solution to (P_n). Then from (6.1) we have

$$\Psi(u_n) = F(u_n) - F(u^*).$$

Since $u_n^l = Ev_n^l \in \partial\Phi(v_n^l)$ we find $v_n^l \in \partial F(u_n^l)$ which implies

$$\langle u_n^l - w, v_n^l\rangle \ge F(u_n^l) - F(w) \quad \forall w \in X^*.$$

Let $k > j \ge 0$ and $\lambda \ge 0$. Then we conclude that

$$\begin{aligned}
e^{\lambda t_n^k}\Psi(u_n^k) - e^{\lambda t_n^j}\Psi(u_n^j) &= \sum_{l=j+1}^{k} \Big(e^{\lambda t_n^l}\Psi(u_n^l) - e^{\lambda t_n^{l-1}}\Psi(u_n^{l-1})\Big) \\
&= \sum_{l=j+1}^{k} \Big\{\Big(e^{\lambda t_n^l} - e^{\lambda t_n^{l-1}}\Big)\Psi(u_n^l) + e^{\lambda t_n^{l-1}}\Big(F(u_n^l) - F(u_n^{l-1})\Big)\Big\} \\
&\le \sum_{l=j+1}^{k} \Big\{e^{\lambda t_n^{l-1}}\Big(e^{\lambda h_n^l} - 1\Big)\Psi(u_n^l) + e^{\lambda t_n^{l-1}}\langle u_n^l - u_n^{l-1}, v_n^l\rangle\Big\} \\
&\le \sum_{l=j+1}^{k} \Big\{e^{\lambda t_n^{l-1}}\, e^{\lambda h}\,\lambda\, h_n^l\,\Psi(u_n^l) - e^{\lambda t_n^{l-1}}\, h_n^l\langle A(v_n^l, v_n^l), v_n^l\rangle\Big\} \\
&\le \sum_{l=j+1}^{k} h_n^l\, e^{\lambda t_n^{l-1}}\Big\{\, e^{\lambda h}\,\lambda\,\Psi(u_n^l) - D(v_n^l)\Big\}.
\end{aligned}$$

Now, in the discrete problems the last inequality is used instead of the Brézis formula (4.3). At first, since the dissipation rate is nonnegative, by setting $\lambda = 0$ we obtain

$$\Psi(u_n^k) \le \Psi(u_n^j) \le \Psi(U) \quad \forall k \ge j \ge 0$$

which means

$$F(u_n(t_2)) \le F(u_n(t_1)) \le F(U) \quad \forall t_2 > t_1 \ge 0.$$

Next, set $R := \Psi(U)$. Since u_n fulfils the invariance property (6.1) and $u_n = Ev_n$, the v_n^l, $l \in \mathbb{N}$, belong to the set M_R defined in Theorem 5.2 and Theorem 5.4, respectively. If we now choose $\lambda > 0$ such that $\lambda e^{\lambda h} c_R \le 1$, these theorems imply that

$$\Psi(u_n^k) \le e^{-\lambda t_n^k} \Psi(U) \quad \forall k \in \mathbb{N}.$$

Then the second assertion of Theorem 6.1 follows easily. $\square$

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